# UNIVERSITY OF TORONTO STUDIES

## PAPERS FROM THE CHEMICAL LABORATORIES

## No. 111: THE EFFECT OF CHLORINE ON PERIODIC PRECIPITATION, BY A. W. FOSTER

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# THE EFFECT OF CHLORINE ON PERIODIC PRECIPITATION

BY MISS A. W. FOSTER

In the course of some experiments on the absorption of ions by colloids, for which the Liesegang phenomenon was used, some interesting results were obtained when chlorinated tap water was used instead of distilled water.[1]

The rings were formed by the action of silver nitrate on a thin sheet of solid gelatine, which had been impregnated with a small quantity of potassium chromate. To a 4 percent gelatine solution was added potassium chromate to make up $\frac{1}{200}$ gram molecular weight per litre. Two ccs of this solution were poured on a glass plate $(3^1/_4'' \times 4^1/_4'')$ kept perfectly level and after the gel had set, a drop of 10 gram molecular weight per litre of silver nitrate solution was allowed to fall on the centre of the gelatine film.

When distilled water was used the resulting ring formation was as shown in Fig. 1, with slight magnification and in Fig. 2, with magnification 25 times. Fig. 3, magnification 25 times, shows the effect produced by using tap water instead of distilled water. As the tap water was known to be chlorinated, it was thought that chlorine might be the cause of the grouping of the rings. To test this, a gelatine solution was made up using pure water, and to part of it was added a drop of the calcium hypochlorite solution used for chlorination (0.960 percent free chlorine). Fig. 2 shows the nature of the precipitate formed in the simple gelatine solution, and Figs. 4, 5, and 6 that of the precipitate formed in the chlorinated solution. It is evident that the chlorine and the grouping of the rings is in some way connected.

When the silver nitrate drop was added to the film a short time after pouring the gelatine on the glass, the rings produced were very close together, both the width of the rings and the spaces between them increasing slightly with

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the distance from the centre (Fig. 4). If, however, the gel was allowed to set for a longer time before the addition of

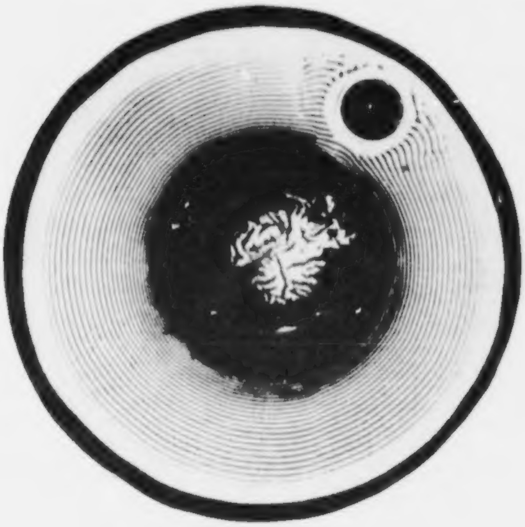

Fig. 1
Diffusion of silver nitrate solution into gelatine solution made with pure water

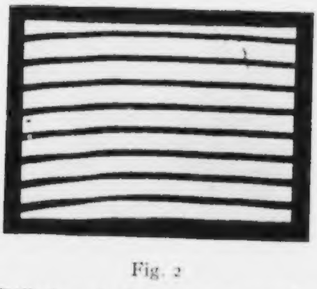

Fig. 2
Diffusion of silver nitrate solution into gelatine solution made with pure water Magnification 25

the diffusing reagent, the rings appeared as in Fig. 5; and if a still greater interval elapsed before the diffusion began the rings were in groups like those of Fig. 6. When the diffusion began at a certain stage in the setting of the gel all trace of

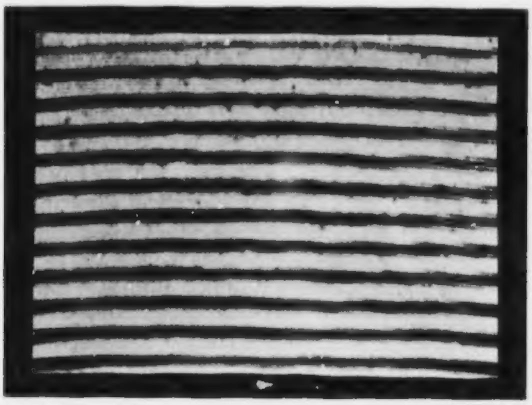

Fig. 3

Diffusion of silver nitrate solution into gelatine solution made with tap water. Magnification 25

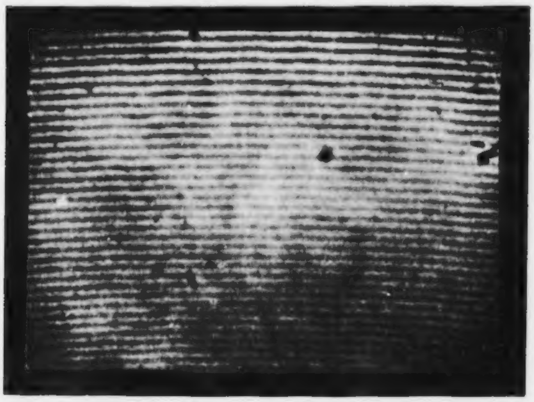

Fig. 4

Diffusion of silver nitrate solution into pure water gelatine solution containing a trace of calcium hypochlorite. Interval between making of film and addition of drop, 1 hour. Magnification 25 the intermediate rings disappeared and the precipitate was in bands made up of groups of rings, the width of each band being, approximately, the same as those produced in the other

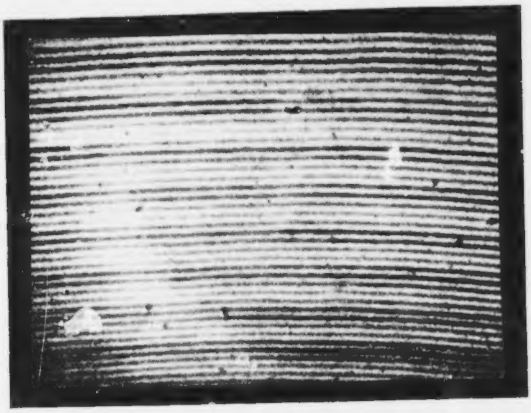

Fig. 5
Same solutions as in Fig. 4 Time interval $1^1/_2$ hours.
Magnification 25

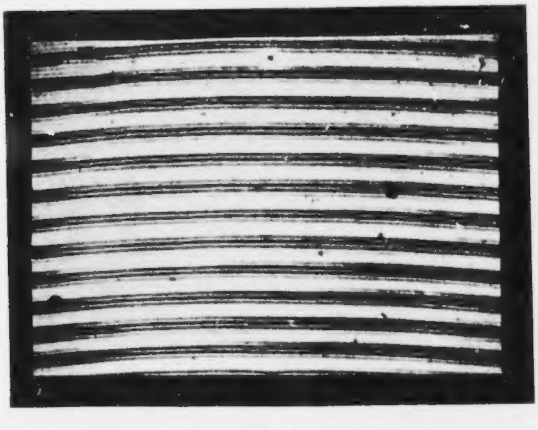

Fig. 6
Same solutions as in Fig. 4. Time interval 4 hours.
Magnification 25

films made from the same gelatine dissolved in pure water and poured out at the same time. The softer the gel, the greater the area of diffusion.

Observations made by means of the microscope during the formation of rings like those of Fig. 4 brought out the fact that the fine bands were to be seen only faintly at first and, under the high power, the tiny crystals could be seen coming into view, the growth of the ring being lateral. Upon these faint bands a second precipitate was formed so that, when diffusion was incomplete, two distinct areas were to be seen, the inner one having rings much darker than the outer one.

For rings obtained by adding the diffusion reagent after a longer time had elapsed from the pouring out of the gelatine, the same kind of thing occurred, except that in the inner area of diffusion, the secondary precipitate formed only on alternate groups of rings (Fig. 5).

The growth of the rings in the film which had set longest before the addition of the silver nitrate drop (Fig. 6) was the same as in the other films, *viz.*, some crystals suddenly appeared in the field of view and in a very short time others appeared beside them so that under the low power the rings were to be seen stretching out lengthwise. These last rings, however, did not form a continuous series but were like those formed last in the softer gelatine, the only difference in their formation being that there were no primary rings upon which the precipitation took place.

In order to show the significance of these results some account of the work which has been done upon the subject of periodic precipitates must be given.

The first explanation, and the one most generally accepted is that due to Wilhelm Ostwald.[2] He said: "By the diffusion of the silver salt into gelatine containing chromate, precipitation does not take place until the metastable limit has passed. This naturally happens in a circle concentric with the drop. Silver chromate in relation to which the neighborhood of the ring is supersaturated, deposits on the precipitate already formed and strengthens it; this continues until the whole of the soluble chromate has been removed from the neighborhood and deposited on the precipitate. The silver salt diffusing on further, supersaturates a new circular strip and the process repeats itself. Since the silver nitrate becomes more dilute by diffusion, the critical concentration at which precipitation begins is reached later and later and the rings form further and further apart."

Morse and Pierce[3] carried on an extended investigation of this phenomenon using capillary tubes and based their explanation upon Ostwald's supersaturation theory. They calculated that when the precipitation takes place the concentrations one seventy-fifth to one two-hundredth of normal for the chromate. They obtained precipitates in pure water but found the rate of diffusion less than for gelatine.

Hausmann[4] suggested that the compounds are present in the colloidal state before supersaturation is reached and precipitation occurs. He showed that the reaction depends only on the ions involved in the precipitate and not on those combined with them and that the speed of the reaction depends on the ion which diffuses into the gel and not upon the one which is present in the gel. He found that $\frac{\text{distance}}{\sqrt{\text{time}}}$ is constant as had Morse and Pierce.

Hatschek[5] used preparations of gelatine containing lead iodide and potassium iodide and diffused a solution of lead into it. The rings of lead were formed as though no lead iodide were already present in the gel which would indicate that supersaturation does not wholly explain the periodicity of precipitates.

Liesegang[6] considered that the spiral forms which he produced in place of concentric rings and which he regarded as being due to some slight disturbance were in no sense at variance with the supersaturation effect. He also showed that a certain amount of acid and gelatose is necessary for the formation of periodic precipitates and that commercial gelatine usually contains these in about the right proportions.

Stansfield[7] worked with gelatine films and in the main the reagents used were potassium chromate and silver nitrate of different concentrations. He strongly endorsed the supersaturation idea and enlarged upon it somewhat; he showed that, according to it, the bands may be equally spaced or at diminishing or increasing distances apart. He emphasizes the fact that the rate of diffusion is an important factor in the formation of rhythmic precipitates.

Bradford[8] proposed the theory that the Liesegang phenomenon might be due to gradual adsorption of the potassium chromate solution in the gel by the growing precipitate so that, the adjacent layers of gel becoming weak in the chromate solution, the silver nitrate would be able to diffuse further into the gel before commencing to form a fresh band of precipitates.

We shall now consider the bearing which the previously described results have upon the theories brought forth by these different workers.

The finer rings are what Liesegang calls the silver chloride precipitates and those of spacing such as is found in gelatine washed in pure water and containing only potassium chromate he calls silver chromate precipitates. In his work the two types seem to have been quite distinct and to have shown no interaction such as suggested by Fig. 5. In the work done to date rings were not obtained in the gelatine solutions except in the presence of the chromate so that the "silver chloride" rings could not be accounted for either on the basis of supersaturation or adsorption as these hypotheses are presented by Stansfield and Bradford. The finer set of bands would seem to have a catalytic effect upon the secondary precipitate so that the characteristic "silver chromate" band is subdivided.

Neither the supersaturation theory nor the adsorption theory takes into account the medium in which the diffusion takes place and that appears from this series of experiments to be of paramount importance. Periodic precipitates were not produced except when the gel was in a particular state. If too much or too little acid was present in the gel the precipitate was uniformly distributed around the central part of the drop because the molecular constitution of the gel is altered

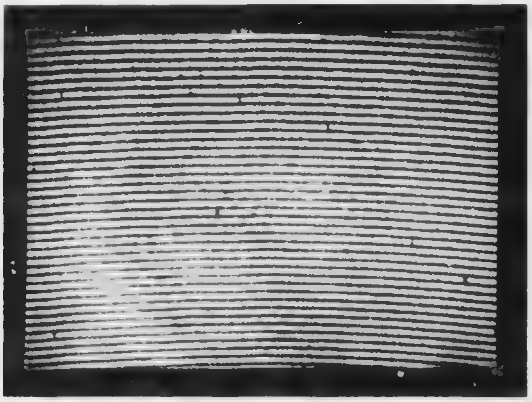

Fig. 7

Diffusion of silver nitrate solution into pure water gelatine solution containing a trace of common salt. Interval between making of film and addition of drop, 1 hour. Magnification 25

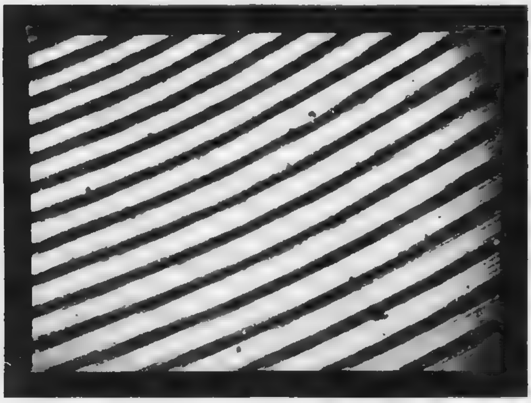

Fig. 8

Same solutions as in Fig. 7. Time interval 3 hours. Magnification 25 so that the rhythmic effects do not appear. That the addition of the trace of the calcium hypochlorite solution or common salt to the gel produces a change of state is evidenced by the fact that gelatine solutions to which these have been added set more quickly than the stock solution and kept longer without liquefying. This change of state is accompanied by a change in the nature of the precipitate. Even the change in the gel due to hydration produces a difference in the rings as is shown in Figs. 5, 6, 7 and 8. Rings were produced in agar when chlorine was present and showed the same spacing as in the gelatine and a certain state of the gel can probably be found such that the precipitates corresponding to the larger rings also appear. Any theory which does not take into account the medium in which the diffusion takes place is not conclusive. For instance, if the gelatine in hardening, forms larger and larger globules, such a circumstance may determine whether the rings are closely spaced as in Fig. 4 or widely distributed as in Fig. 6.

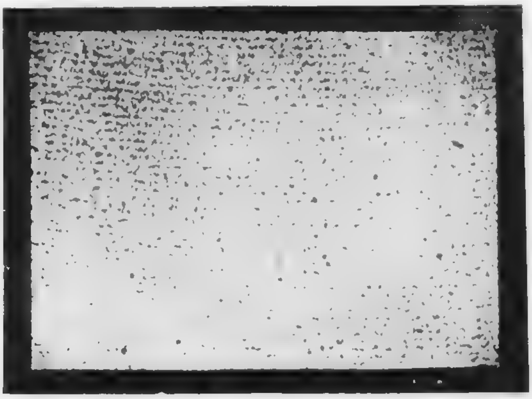

Fig. 9

Silver nitrate diffusing into pure agar water solution containing trace of calcium hypochlorite

TABLE 1
Explanation of Figures Accompanying the Paper

| Figure No. | Magnification | Contents of the gelatine solution | Time between formation of film and addition of nitrat | Character of the precipitate |
|---|---|---|---|---|
| 1 | 1.5 | Gelatine, distilled water and potassium chromate | Characteristics independent of this interval | Single wide rings decreasing in width with distance from the centre |
| 2 | 25 | Same as above | Same | Same |
| 3 | 25 | Gelatine, chlorinated tap water and potassium chromate | 3 hours | Rings in groups of three, spiral in form |
| 4 | 25 | Gelatine, distilled water calcium hypochlorite solution and potassium chromate | 1 hour | Narrow rings, close together, formed by two precipitations |
| 5 | 25 | Same as 4 | 1$^1/_2$ hours | Narrow, faint rings close together alternating with darker rings formed by two precipitations |
| 6 | 25 | Same as 4 | 4 hours | Dark rings in groups of three or four, spiral in form, formed by a single precipitation |
| 7 | 25 | Gelatine, distilled water common salt and potassium chromate | 1 hour | Rings similar to those in 4 but darker and narrower |
| 8 | 25 | Same as 7 | 3 hours | Rings of the secondary set in two or threes rather than threes or fours as in 6 |

This work was carried out under the direction of Professor E. F. Burton.

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